Memo to: Anne Monnelly, DCR

From: Naomi Slagowski and John Durant, Tufts University

Date: 11 September, 2006

RE: Lake Cochituate Solarbee Study

The purpose of this memo is to describe our plan for water and sediment sample collection in Lake Cochituate, QA/QC measures, and analysis methods.

1. Hypotheses

Our working hypotheses are that the SolarBee circulators may:

(1) limit the availability of one or more critical soluble nutrients (possibly nitrogen or phosphorus) from either the water or the sediment

> a) By changing the dissolved oxygen content and/or temperature in the water column, increased water circulation directly impacts plants. Test with DO and temperature profiles at transects away from mixers and in control sites. Also include full suite of typical hydrolab parameters in profiles (pH, conductivity, TSS, alkalinity, Chlorophyll-a).
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> b) Circulators improve mixing of dissolved oxygen throughout the water column, which in turn favors nitrification of NH4 in the sediments and water column resulting in impacts to plants. Measure NH4, NO2+NO3, total iron, SRP and TP in transects and controls in the water column and sediment porewater.
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> c) Circulators increase DO causing oxidation of iron and precipitation of available phosphorus. Measure total iron and TP in water. Include combined nitrite/nitrate, SRP and TP in the sediments.

(2) cause increase in turbidity either by resuspension of bottom sediments or by increasing growth of phytoplankton and periphyton thus leading to light limitation of milfoil. Measure Secchi depth and turbidity as well as chlorophyll-a at all sites; also inspect plants for accumulation of sediment, iron or excessive periphyton growth on leaves that could cause light limitation.

2. Sampling plan

Test and Control Sites

Sampling locations in the Middle and South Ponds of Lake Cochituate were determined in consultation with Department of Conservation and Recreation staff with input from residents who live near the lake (Figures 1 and 2). One pair of sites (control and test site) is located in Middle Pond and another pair is located in the South Pond. The Middle Pond sites are in two

adjacent shallow coves that are separated by a narrow point of land that projects into the lake (Figure 1). The South Pond sites are located in areas heavily populated by invasive plants. These sites are along the same length of shore and have similar conditions and plant growth. The location of these sites was deemed far enough from the inflow from Fisk Pond that the water movement would not affect the sites. South Pond was of special interest to residents because the plant infestation is quite heavy in that pond, and it is used extensively for recreation.

Horizontal Transects

At each of the four sites, two moorings will be set in the Eurasian watermilfoil beds perpendicular to the Solarbee site along the shore, and up the shore away from the Solarbee. Each transect will be 70 m in length, marked at either end with buoys. At the start of each sampling session a graduated line will be tied off to each mooring thus defining the transect. The boat will be moved along the transect so that samples can be collected at prescribed distances and depths. Water quality measurements and samples will be taken at 0, 35, and 70m intervals along the transect (Figure 3). Water quality samples will be taken at the surface and near the sediment/water interface, the depth and number of samples depending upon depth and water chemistry at sampling site.

Water column samples

Water samples will be collected at each site along a given transect. To characterize the change in water chemistry as a function of depth, an adaptive sampling approach will be used to determine at what depths to collect the samples. Thus, if one end of the horizontal transect is very shallow and well-mixed, we will collect one sample at depth (in addition to the one at the surface); however, if at a deeper site the water column is stratified, as many as four or five samples will be collected at depth, particularly below the thermocline. (Figure 2) Water samples will be collected from the lake using a peristaltic pump fitted with inert tubing that is marked at 1m intervals. The tubing will be lowered to the desired depth and water from that depth will be pumped for two minutes to clear the line of previous water. Water for Total Suspended Solids, Turbidity and Alkalinity will be pumped into 1L and 250mL bottles, then rinsed and filled. Water for Phosphorus, Ammonia, Nitrates/Nitrites and Iron will be filtered in the field using a 0.45µm in-line filter attached to the peristaltic pump tubing. This filtered water will be used to rinse the bottles for Phosphorus, Ammonia and Iron and the bottles filled. Total Iron water samples will be fixed in the field with nitric acid. All water samples will be stored on ice in coolers on the boat until return to the laboratory. Upon return to the laboratory, a small aliquot of water will be taken to be filtered through 0.2µm filters for Ion Chromatography analysis of anions including Nitrates/Nitrites. Water for phosphorus analysis will be fixed with hydrochloric acid. All water will be stored at 4°C, except for water for ammonia analysis, which must be frozen. Vertical profiles of temperature, pH, conductivity, dissolved oxygen, and Chlorophyll-a will be measured with the field probe to help determine how many samples to collect at depth at a particular site.

Sediment Porewater Samples

Sediment porewater "peepers" will be used to measure phosphorus, ammonia, nitrates/nitrites and iron concentrations in sediment porewater. An underwater float will be placed at each sediment sampling location. Peepers will be constructed of HDPE bottles filled with high purity deionized water and covered with a semi-permeable polysulfone membrane (0.2 µm pore size).

Polysulfone membranes are used because they are resistant to bacterial degradation. Peepers will be constructed of a PVC pipe with an open bottom to aid driving into sediment. Bottles will be fit into holes drilled in the pipe to obtain measurements at different sediment depths. Bottles will be placed at approximately 2 cm intervals until a depth of approximately 20cm into the sediment, for a total of at least 10 peeper ports below the sediment-water interface. They will be placed in the sediment at each site, and will be left in the sediment to equilibrate for about one month. Peepers will be placed in the sediment just before Solarbees are turned on, and pore water samples will be taken after one month, and again approximately six months and one year after the Solarbees have been running.

Plant Survey
Plant surveys will be conducted by tossing a 0.5x0.5m square into the milfoil bed at two points randomly in each transect. In this square, all rooted plants will be harvested and transported back to the laboratory. In the lab, total aquatic vegetation mass will be determined, along with total milfoil mass. Milfoil dry weight will also be determined. Plant surveys will be conducted prior to Solarbee installation day, and again in the spring and summer following installation.

3. QA/QC

Pre-field QA/QC
The YSI 6820 sonde will be calibrated with standard solutions for pH, conductivity, dissolved oxygen, oxidation/reduction potential and chlorophyll. Sampling bottles and tubing will be acid-washed prior to use. In addition, all sampling bottles will be triple-rinsed before sampling to remove residual impurities.

Field QA/QC
Coolers will be transported to the field with freezer packs and/or ice to keep samples cool. One duplicate sample will be collected on each sampling day to assess reproducibility in sampling technique. Field blanks will be collected each sampling day by pumping deionized water through the sampling and filtration equipment after sampling has occured. The analysis of field blanks will allow measurement of chemicals leaching from tubing, filters or bottles.

Laboratory QA/QC
Each analytical test will be accompanied with laboratory blanks of Milli-Q or deionized water, using the same reagents and glassware to ensure that no interferences are introduced by glassware, reagents or methods. As is recommended in Standard Methods (1) for every 10 samples analyzed, a lab replicate will be performed to ensure reproducibility. Analyses will be performed "blind" where either randomly numbered flasks will be used, or a lab assistant will record actual sample identification and the analyst will be unaware of sample identification. The same is true for lab replicates. In this way, no analyst bias could be introduced into the analysis of samples. All laboratory analyses will be performed according to Standard Methods (1).

4. In Situ Measurements

T, pH, Conductivity, Dissolved Oxygen, Oxidation/Reduction Potential and Chlorophyll-a

In situ measurements of temperature, pH, dissolved oxygen, conductivity, oxidation/reduction potential and chlorophyll-a will be made using a YSI 6820 field probe that will be lowered to prescribed depths.

Chlorophyll-a

A chlorophyll-a probe will be obtained to attach to the YSI 6820 sonde in September, 2006. The first day of sampling, chlorophyll samples will be obtained by field filtration, according to standard methods. Filters will be wrapped in foil to protect samples from light, and frozen for up to three weeks before analysis. Chlorophyll probe measurements will be calibrated against field-filtered samples done by extractive analysis, Standard Method 10200 H: Chlorophyll.

5. Sample Analysis

Total Suspended Solids

Immediately upon returning to the lab after collecting water samples, water will be transferred to a refrigerator at 4°C. Within 24 hours of sample collection, total suspended solids will be determined by Standard Method 2540 B: Total Solids Dried at 103-105°C. Filters will be pre-rinsed, dried, desiccated and weighed before sampling to facilitate TSS analysis.

Alkalinity

Immediately upon returning to the lab after collecting water samples, water will be refrigerated at 4°C. Within 24 hours of sample collection, alkalinity will be determined on using Hach Chemical Company Alkalinity Test Kit, Model AL-DT, with digital titrator. This kit has been chosen as opposed to standard methods, since the amount of time necessary to perform standard alkalinity measurements, along with the short amount of hold time and number of samples collected would make it physically impossible to complete the measurements before the hold time expires. The accuracy of the tests is stated to be ±1%. This accuracy will be checked by analyzing lab blanks and laboratory replicates for every 10 samples. Alkalinities will be tested after allowing samples to warm to room temperature, as stated in Standard Methods.

Turbidity

Turbidity readings will be performed within 24 hours using an HF Scientific, Inc. DRT 1003 Turbidimeter, following normal blank and replicate procedures. Depth of light penetration will also be measured in the field using a Secchi disk.

Phosphorus

Filtered (0.45 µm) water collected for phosphorus analysis will be fixed with hydrochloric acid and refrigerated at 4°C. Phosphorus will be determined by Standard Method 4500-P E: Ascorbic Acid method (a.k.a. EPA Method 365.3). Reagent blanks, laboratory replicates and a known concentration spike will be analyzed along with samples. As a result, reagent interferences will be eliminated and recovery efficiency can be determined. The phosphorus analysis will be performed within 28 days of sample collection.

Ammonia
Filtered (0.45 µm) water for ammonia analysis will be frozen upon return to the lab and analyzed within 28 days. Water will be analyzed using Standard Method 4500-NH_3 F: Phenate Method. Normal laboratory blanks and replicates will be analyzed.

Nitrate + Nitrite
Filtered (0.45 µm) water will be again filtered through 0.2 µm filters upon return to the lab, and immediately analyzed using Ion Chromatography based upon Standard Method 2110 B: Ion Chromatography with Chemical Suppression of Eluent Conductivity, and method development recommendations from the IC manufacturer, Dionex Corporation. The chromatograph will be an integrated reagent-free system using an IonPac AS18 Anion-Exchange Column, with peak integration performed by Dionex "Chromeleon" software. Blanks, 10% replicates and % recovery spike samples (also every 10%) will be run during each analysis. Samples will be kept cold while standards are being prepared for the run. Recovery percent should be between 90 and 100%. The anions measured by ion chromatography will be: chloride, nitrite, nitrate, carbonate, sulfate and phosphate.

Total Iron
Filtered (0.45 µm) water for iron analysis will be fixed in the field with nitric acid. Upon return to the lab, the water will be refrigerated at 4°C, and analyzed within six months according to Standard Method 3111: Atomic Absorption.

1. Eaton, Andrew D., Clesceri, Lenore S., Rice, Eugene W. (Eds.) *Standard Methods for the Examination of Water and Wastewater* (21st edition). American Public Health Association. Washington, D.C.

2. Teasdale, Peter R., Batley, Graeme E., Apte, Simon C. (1995) "Pore water sampling with Sediment Peepers." *Trends in Analytical Chemistry*. 14(6): 250-256.

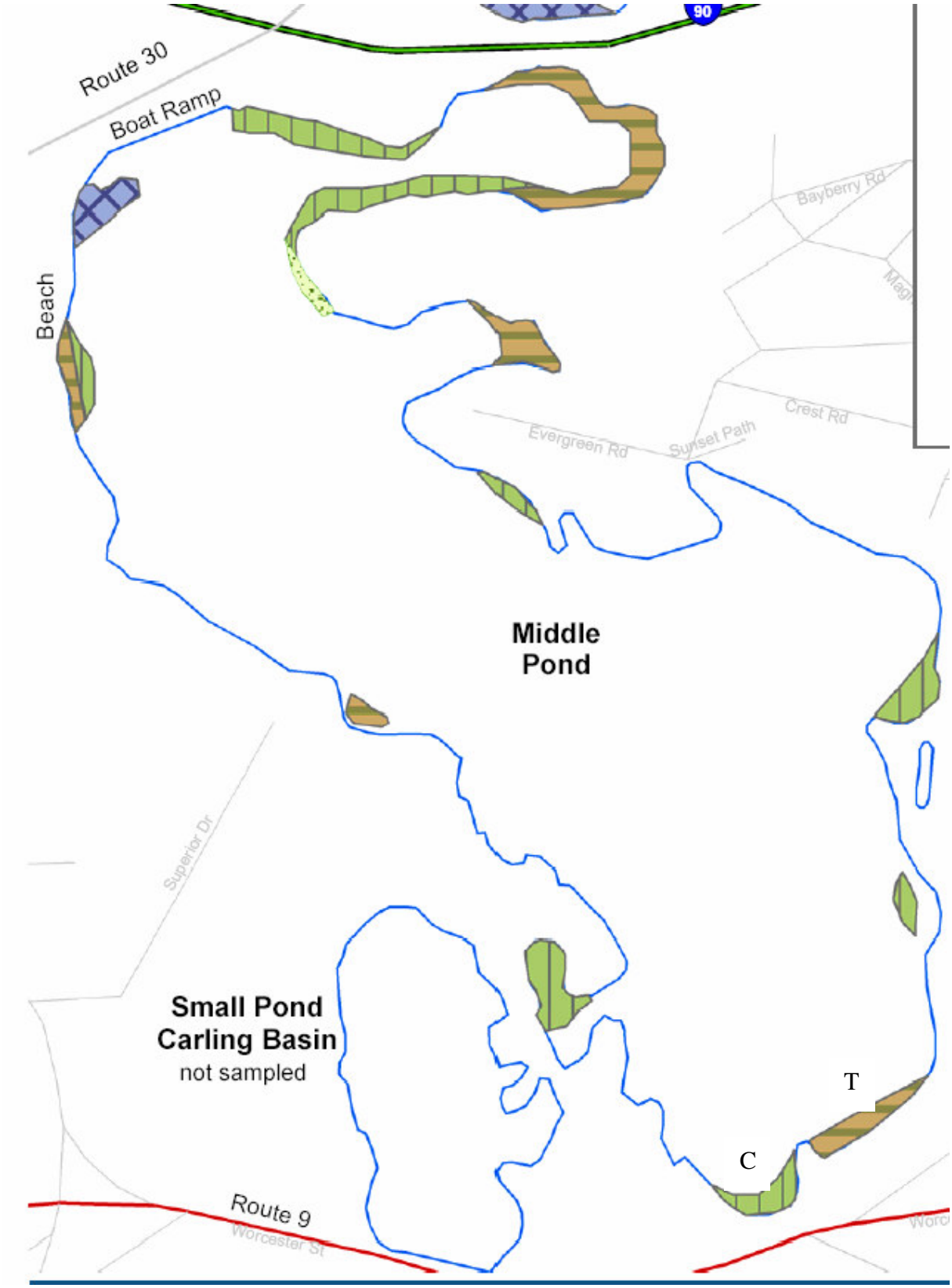

Figure 1. Middle Pond control (C) and test (T) sites. Plant density map by ENSR and AECOM.

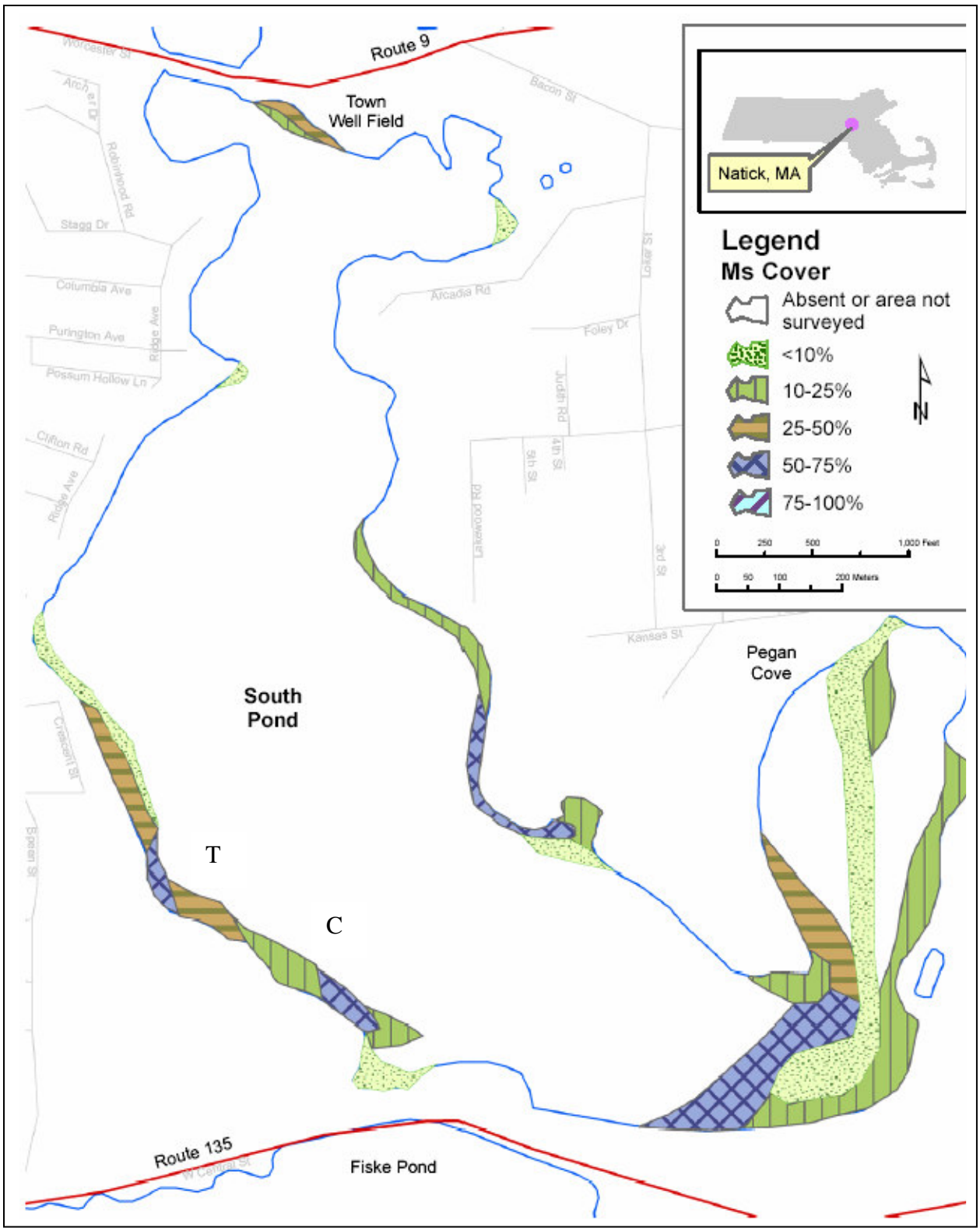

Figure 2. South Pond control (C) and test (T) sites. Plant density map by ENSR and AECOM

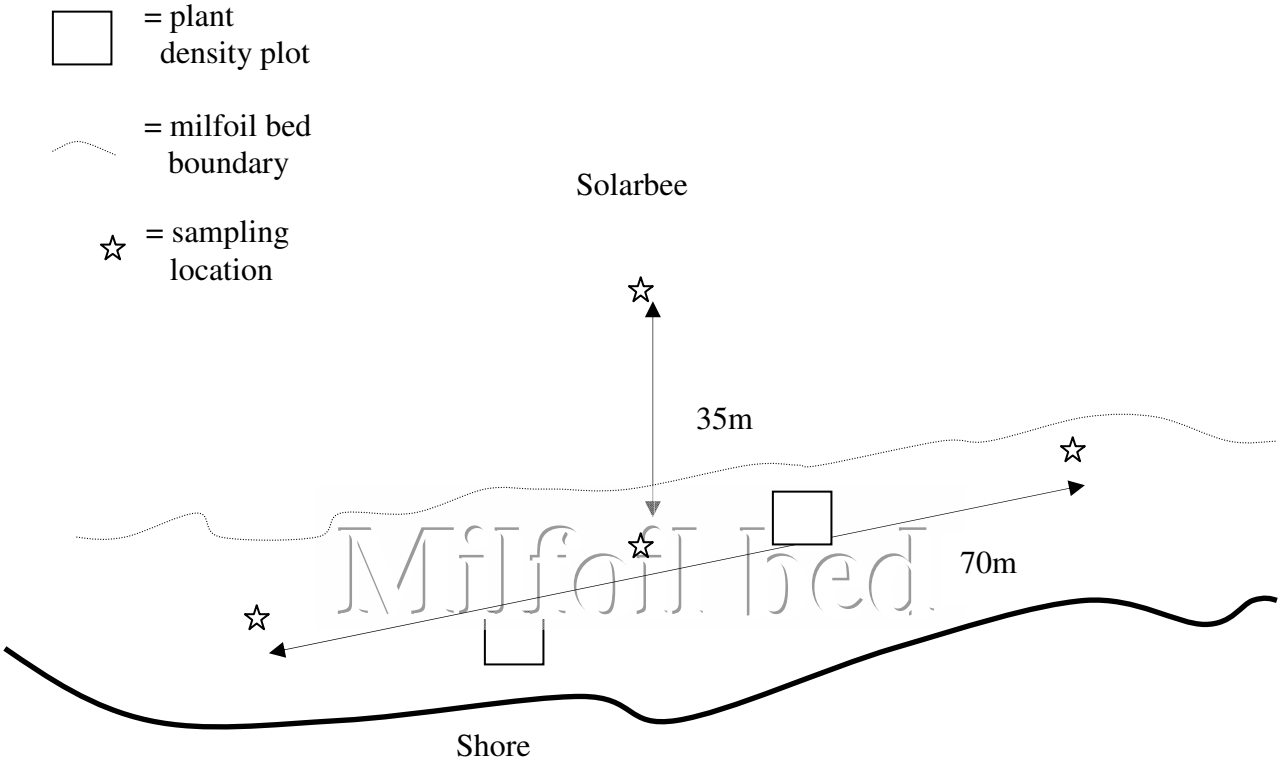

Figure 3. Sampling locations at control and experimental sites.